William Marsh Rice University

Houston, Texas

Semi-Annual Status Report #28

on

NASA Research Grant NGR-44-006-001

covering

Research on Materials for Advanced Electronic

and Aerospace Application

for the period

January 1, 1973 - June 30, 1973

Under the Direction of

C. D. Armeniades

F. R. Brotzen

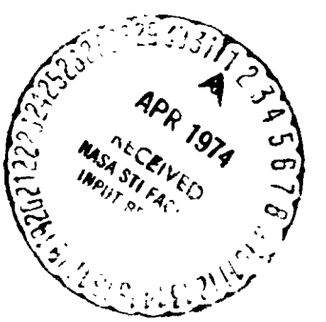
T. L. Estle

J. R. Margrave

H. E. Rorschach

and

M. L. Rudee



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I. Introduction

During the last three years, the work supported by the NASA Materials Grant has evolved into a concentration in three principal areas:

1. Data processing (optical and magnetic)
2. Hydrogen in Metals and Stress-Corrosion Phenomena
3. Polymers and Materials at High Temperatures and Pressures.

These general areas were chosen after a series of working conferences intended to identify NASA problem areas related to the competence of the investigators in solid materials at Rice University. These conferences are listed below:

1. Conference on Photochronism (NASA Washington, Aug. 20, 1970)
2. Conference on Hydrogen Embrittlement (NASA Lewis, April 16, 1971)
3. Conference on Polymers (NASA Lewis, Oct. 16-18, 1972)

Since the time of these conferences, the funds of the NASA Materials Grant have been distributed to support research that can contribute to the solution of the fundamental problems in these areas.

As a consequence, 15 faculty members in 5 departments received support for the research described in Section II of this report. Also participating were 11 graduate students (3 foreign) and 5 postdoctoral fellows (2 foreign). The publications reporting past work in the areas supported by this grant are given in Appendix I.

The research programs supported by the grant have been oriented toward a fundamental understanding of the solid-state materials science involved in the three major areas of interest. Our intention for the future is to make this research more problem-oriented, and for this purpose it will be necessary for us to establish much closer contact with those NASA groups working in these areas. Our next proposal will describe the methods by which we hope to increase the strength of the interaction with the NASA working groups and to increase the emphasis on problem-related research programs.

A financial statement covering the period of this report is given in Appendix II.

Research Reports

A. Data Processing

Staff: H. C. Bourne, Professor of Electrical Engineering
T. L. Estle, Professor of Physics
R. C. Minnick, Professor of Electrical Engineering
T. A. Rabson, Professor of Electrical Engineering
M. L. Rudee, Associate Professor of Materials Science
F. K. Tittel, Associate Professor of Electrical Engineering

1) Optical Information Storage

As the speed of current computers increases, the amount of data which can be processed increases. The ultimate capacity of practical computers is thus often determined by the storage density, access speed, and cost of the memory system. One of the most attractive of the alternatives for new memories is optical storage. In particular the three-dimensional phase holographic storage possible in electrooptic crystals could lead to significant reductions in cost and increases in speed and density. However, progress in developing such optical memories is severaly hampered by a lack of understanding of the basic solid state processes involved. This in turn impedes the development of memories with characteristics as good as those needed (characteristics which in principal seem realizable). The goal of this research is to provide the basic understanding necessary for the future development of this technology.

Two complementary research programs are exploring this subject. One is carried out in the Physics Department under Professor T. L. Estle and the other in the Electrical Engineering Department under Professors T. A. Rabson and F. K. Tittel. Both programs have studied primarily lithium niobate ($LiNbO_3$). In $LiNbO_3$, and other ferroelectric crystals, the phase holograms which result when laser beams interfere in the crystal are caused by the following chain of events: photoionization of defects in the crystal, motion of the charge carriers, and trapping of the carriers at defects. If the carriers are electrons the regions of constructive interference (high light intensity) become positively charged and the regions of destructive interference (low intensity) become negative. The linear electro-optic effect causes the resulting space charge to manifest itself as changes in the refractive indices and a phase hologram is produced.

The studies of $LiNbO_3$ in the Physics Department have been primarily on deliberately-doped crystals. The sensitivities of $LiNbO_3$ crystals singly doped with Ti, Cr, Mn, Fe, Co, Ni, Cu, Er, or U have been measured. Many of the sensitivity measurements have been made as a function of the wavelength and the polarization of the argon ion laser used to write the holograms. Polarized optical absorption spectra were obtained for all of these crystals. Of the nine dopants studied, the best sensitivities were obtained for Mn, Fe, and Cu doped crystals. These three samples have sensitivities which are two to three orders of magnitude better than the purest undoped $LiNbO_3$ studied in this laboratory. All three have sensitivities comparable to the best reported values.

The sensitivity is observed to increase as the wavelength decreases. In addition the sensitivity is usually least where the impurity induced optical absorption is largest since the absorption seems to take light from the incident beams with little or no compensating increase in photoionization efficiency. It would appear feasible to increase the sensitivity of iron-doped material by about another order of magnitude by going to a shorter wavelength than the 488 nm. line of an argon ion laser. An increase in sensitivity by adjusting the Fe^{3+} to Fe^{2+} concentration should combine with the wavelength dependence and the present measured sensitivity to imply a possible sensitivity of iron-doped $LiNbO_3$ which would be five orders of magnitude greater than for pure $LiNbO_3$.

In order to extend the studies of doped $LiNbO_3$ to impurities presently unavailable, diffusion of impurities into $LiNbO_3$ crystals is being attempted. Crystals doped with copper by diffusion have identical electron paramagnetic resonance (EPR) spectra to the crystals doped in the melt and studied earlier. (These latter crystals were purchased from Isomet. Rice has no facilities for growing the required crystals.) No other measurements have yet been made on the crystals into which copper was diffused. A $LiNbO_3$ crystal was also doped with silver by diffusion and preliminary EPR experiments suggest that the silver also is present in the crystal, although the spectra have not been explained as yet.

All copper-doped $LiNbO_3$ crystals show a complicated anisotropic EPR spectrum resulting from the copper. For a long period of time it

was not clear whether the copper was associated with another defect or whether a spontaneous distortion occurs because of the Jahn-Teller effect. The latter may manifest itself as a static or dynamic distortion or something between these extremes. The latter seems to be the case.

Studies of other electrooptic crystals have been started. Early measurements on potassium and ammonium dihydrogen phosphate (KDP and ADP) did not reveal a measurable sensitivity for writing phase holograms. The ADP studied was pure and also doped singly with Mn, Fe, or Cu. The KDP was pure. Although these crystals are electrooptic, they are not ferroelectric at room temperature. Therefore the measurements were made both with and without a large applied electric field.

The program in the Electrical Engineering Department continued to focus on the use of pulsed lasers to write phase holograms in $LiNbO_3$. Writing with pulse trains was reported in Semi-Annual Status Report #27. Holograms have now been written with a single pulse of 30 to 75 nanosecond duration. A pulse at 694.3 nm. from a Q-switched ruby laser and a pulse at 531 nm. from a frequency-doubled Nd:glass laser were used to write in iron doped $LiNbO_3$. The recording sensitivity for these 3×10^{-8} sec. pulses is better than the estimates made using CW lasers. Clearly there is no intrinsic time constant limiting writing speeds greater than about 10^{-8} sec.

The sensitivity of the iron doped crystal was measured as a function of wavelength. The high sensitivity was ascribed to the high Fe^{2+} concentration and the relatively low Fe^{3+} concentration.

2) Magnetic Recording Materials

Although radically new technologies, such as optical storage, may someday drastically alter the approach to storing data, there is a strong likelihood that existing technologies will evolve so as to maintain their importance. The oldest and most important of the existing technologies is magnetic recording which has recently undergone a significant change in direction with the advent of bubble memories and particularly with the recent development at IBM of amorphous materials for magnetic bubble memories.

Thin magnetic films made from certain materials will, when of the proper thickness, support magnetization in a direction perpendicular to the plane of the film. In general, the state of the film is such that the direction of the magnetization is about equally divided between areas of upward-pointing and downward-pointing magnetic field vectors. These areas are called domains, and they are distributed throughout the film in a serpentine or maze-like random pattern. When a DC magnetic bias field is applied, also perpendicular to the film, those domains which are aligned parallel to the field grow in area, while those which are anti-parallel, decrease in size. In some of these materials, under the proper conditions of bias field and temperature, the anti-parallel domains will collapse into stable disc-like islands called bubbles. Because of the high packing densities (10^6 bits per square centimeter) and high data rates (10^6 Hertz) which can be achieved in memory devices utilizing bubbles as bits, considerable interest has developed in those materials which will support bubble structures.

The two research programs at Rice in this area are now directing their efforts toward the study of amorphous materials for magnetic bubble memories. One program is in the Electrical Engineering Department under the direction of Professors H. C. Bourne and R. C. Minnick and the other is directed by Professor M. L. Rudee in the Materials Science group of the Department of Mechanical and Aerospace Engineering and Materials Science.

The recent work in the Electrical Engineering Department has concentrated on two major areas. The first was the study and analysis of bubble propagation circuits. Of the several methods possible for moving bubbles within a bubble material, the external excitation of a permalloy overlay propagation circuit has had the most success. Design of these circuits has been more or less intuitive, and actual analytical studies of their properties have proven to be quite difficult. The static theoretical circuit model was extended to include a rotating drive field. From this, a computer simulation determines energy profiles for a bubble interacting with the drive circuit. The position of minimum energy is the position of the bubble, and thus the motion of the bubble itself along the propagation circuit can be determined as a function of external drive field. Studies of the T-bar pattern, one of the more commonly encountered circuits, were made using this technique. The effects of varying such circuit parameters as the pattern width, and the spacing between the circuit elements could be easily observed. Those factors which were primarily responsible for limiting propagation speed could be

determined, and criteria for optimum circuit design were obtained. Extending the principles which evolved from this computer simulation, a field access circuit of substantially different character from previously fabricated circuits was designed. This circuit was built and tested, and showed an essentially uniform bubble velocity profile, one of the primary requirements of a high-speed, wide-margin propagation circuit.

The other area is the study of magnetic bubble materials. As reported last time, the announcement by IBM of the discovery of an amorphous metallic film composed of Gadolinium and Cobalt which will support magnetic bubbles has caused the research to turn toward this new class of bubble materials. Substantial progress has been made towards achieving the capability of preparing these films. A sputtering apparatus was constructed, and is now operational. Several different kinds of Gd-Co films have been sputtered on glass substrates, and are now undergoing investigation. In order to carefully study and evaluate the films as they are produced, the capabilities for determining their composition by X-ray fluorescence, for measuring their magnetic properties with a high-current B-H loop tracer, and for observing domain formation and propagation through the polar Kerr effect have been developed. An electron-beam furnace was constructed for fabrication of tungsten-backed sputtering targets of varying materials composition. Work is now in progress for the development of a vacuum system in which magnetic films can be produced by the simultaneous evaporation of two materials from separately controlled electron gun sources.

The research directed by Professor Rudee concerns amorphous materials. Part of this work is now being directed to the study of amorphous magnetic bubble materials in close collaboration with the group in Electrical Engineering. The present efforts are directed toward preparation of films that duplicate the properties reported by IBM. Once this has been accomplished systematic studies of the dynamic and static properties of these films will be undertaken. Conversations with members of the IBM research lab. indicate that our present efforts at duplicating their work are going as well as anybody's in the country. However, we have not yet been completely successful. Due to their enormous commercial promise IBM is not revealing much about the actual preparation techniques that they have found successful.

The remainder of Professor Rudee's work concerns the study of amorphous semiconductors by electron microscopy. When a va of a semiconducting material is condensed onto a substrate, it is often observed that the material forms an amorphous rather than a crystalline structure, and some of these amorphous materials have interesting switching and memory applications. The materials of commercial interest are usually binary and ternary compounds. In order to provide a basis for understanding these more complicated structures, a considerable research effort has been focused on understanding the properties of elemental amorphous germanium and silicon. The strategy was the application of electron microscopy to the study of the structure of amorphous germanium and silicon. The results of these studies have indicated that amorphous germanium and

silicon have a greater degree of atomic order than had been detected by other techniques. During this reporting period, a simple but nevertheless illuminating experiment has been performed which again indicates that there is more order than was supposed in the continuous random network hypothesis. The motivation for this experiment came from reports from Stanford that the properties of amorphous germanium could be altered by vapor depositing the material at 45° from normal incidence. Nearly simultaneously Bell Labs reported that the electrical conductivity in amorphous germanium was anisotropic. These two reports suggested that it might be valuable to examine structural anisotropy in amorphous germanium. Films were produced at both normal incidence and at 45° incidence and a significant difference in the diffraction patterns was measured. From these observations it can be concluded that there exists some anisotropic structural feature in amorphous germanium, and that this feature can be oriented during the deposition process. This observation clearly is at variance with the standard random network hypothesis which assumes that the structure and the atomic arrangements within it are isotropic.

3) Tunable Infrared Sources of Coherent Radiation

In a program directed by Professor F. K. Tittel, a tunable source of coherent infrared radiation has been developed. This source produces pulsed radiation in the kilowatt power range continuously tunable over the wavelength range from 3.2 μ to 7.3 μ. This has been accomplished by difference frequency generation as a result of mixing two laser beams in a phase-matched nonlinear crystal (proustite). Two schemes are employed: One method involves the

optical mixing of a wavelength tunable dye laser and its fixed frequency ruby pump while the other relies on optical mixing of two dye lasers pumped by the same ruby pump laser. In principle use of dual dye-laser mixing allows the production of difference frequency radiation from about 5u to the far infrared assuming the existence of appropriate mixing media.

A Q-switched ruby laser (output power: 900 kw, pulse duration: 25 nsec, TEM_{oo} mode) is split into two beams with orthogonal polarizations. The approximately 500 kw power of the horizontally polarized component pumps an efficient narrow linewidth organic dye laser. The optical mixing of the two laser beams (ruby and dye) occurs in 1 cm long proustite crystals. The second scheme for generation of mid-infrared radiation is by optical mixing of two dye lasers pumped by a common ruby laser pump (4 Mw). Dye laser #1 (HEXA in DMSO) produces a horizontally polarized output of 120 kw pulses (< 3Å) in the wavelength range 8400 to 8500Å. A vertically polarized output of 200 kw pulses (< 5Å) is obtained from dye laser #2 (OXA in DMSO) in the wavelength range 7450 to 7800Å. The two dye laser beams are recombined by a dichroic reflector and focused into a proustite crystal, which is appropriately oriented for optimum phase-matched mixing of the two dye laser outputs.

B. Hydrogen in Metals and Stress Corrosion Phenomena

Staff: F. R. Brotzen, Professor of Materials Science
C. G. Harkins, Senior Research Chemist in Materials Science
N. F. Lane, Professor of Physics
R. B. McLellan, Associate Professor of Materials Science
J. R. Roberts, Professor of Materials Science
H. E. Rorschach, Professor of Physics

The past few years have seen an unprecedented upsurge of interest in the physics, chemistry, and technology of metal-hydrogen systems. This occurrence results from the increasing realization of the role played by hydrogen in many phenomena of vital importance in physical metallurgy such as embrittlement and stress corrosion cracking, where the presence of very low concentrations of hydrogen atoms can disastrously impair the mechanical properties of construction materials. In addition to the technological significance of hydrogen-metal systems, it is also apparent that their study can throw much light on some of the basic problems of solution theory. The relatively large mobility of the hydrogen atom in many metals enables equilibrium thermodynamic measurements to be made over much larger temperature ranges than is otherwise possible. This enables very accurate measurements of interaction energies and entropies to be made. These data can be correlated with the electronic structure of the solvent metal. In addition to the large temperature range, many metals dissolve very large amounts of hydrogen, yielding data uniquely suitable for studying the nature of the interactions

between solute atoms. The work being undertaken at Rice encompasses a broad range of studies ranging from theoretical considerations of the interatomic potentials in the neighborhood of a dissolved hydrogen atom to the effects of dissolved hydrogen on the mechanical properties of metals and alloys.

A high degree of cooperation exists between the individual members of the research team and indeed some of the research projects were planned as the result of discussions involving all the researchers.

Dr. N. F. Lane is undertaking a theoretical study directed toward understanding the effects of hydrogen on various properties of metals. Residual resistivities of metals containing small concentrations of hydrogen provide one type of probe on the effect of a hydrogen atom on the local electron density. Previous theoretical calculations based on the linearized screening model are in semi-quantitative agreement with resistivity measurements. The present effort is directed toward refining these calculations by taking into account the effects of density oscillations (Friedel Oscillations) on the scattering phase shifts and thus the momentum-transfer cross sections which enter into the resistivity calculations. Preliminary results show that the effect of including Friedel Oscillations will be significant and should lead to a much improved description of the electron scattering and thus an improved theory for the residual resistivity.

Dr. H. E. Rorschach is also engaged in a fundamental study of the nature of the interaction of a proton with the lattice ions and the band electrons so that a more basic understanding of hydrogen diffusion and solubility in metals can be obtained. In this work the interaction of the proton with the electrons is studied by considering the effect of dissolved hydrogen on the superconducting transition and electrical resistivity. An eddy-current technique has been developed for measuring the electrical resistivity of ultrapure metal samples. Measurements have been made on pure single crystals of Mo and Re and on Mo + H specimens. The object of this work is to investigate the clustering of hydrogen atoms during cold-work by observing the concomitant resistivity changes.

In addition to the work directly related to clustering, Dr. Rorschach is also investigating several theoretical problems of considerable interest for a basic understanding of hydrogen-metal solutions. These problems encompass the importance of the "Wigner Condensation" for protons, the possibility of an attractive component in the proton-proton interaction due to the presence of phonons. If this is the case, the possibility of protonic superconductivity must be considered. Since the above interactions affect the transport properties of hydrogen in metals, experiments are also being designed in which semi-permeable membranes and potentiometric techniques will be used to measure proton concentrations and mobilities in metals.

Dr. R. B. McLellan is investigating the interaction of hydrogen in metals from the standpoint of thermodynamics and statistical mechanics. Despite the relatively large bulk of thermodynamic data referring to hydrogen-metal solutions, significant gaps in the knowledge occur. An experimental program aimed at filling some of these gaps is underway. The H-solubility of a series of metals as a function of temperature is being measured with respect to H_2-molecules at atmospheric pressure. The "equilibrate-quench-analyze" technique is being used. The high mobility of hydrogen in metals enables equilibria spanning a wide temperature range to be measured, so that the analysis of the solubility data yields accurate data for the energy and entropy of a dissolved hydrogen atom. Such measurements have already been made for the solutions of hydrogen in Mo, Ni, Ir, Rh, Ru, Cu, Au, Ag, Cr, W and Al. Current measurements are being made of the solubility of hydrogen in the "binary" metal solvents Fe + Cr and Fe + Ni. These systems are of interest in view of the possible correlation between the energy needed to dissolve a H-atom and the electronic structure of the solvent solution. Furthermore, highly stable low-temperature superlattices appear in the systems Fe_3Ni and Fe_3Cr so that the possibility of forming ternary superlattices exists.

Other experimental work is centered on measuring the composition variation in the elastic properties of hydrogen-metal solutions at high temperatures. Such information is necessary to enable a comparison to be made between the results of statistical mechanical

models for solid solutions (which normally assume constant volume) and measured partial thermodynamic functions (measured at constant pressure).

Theoretical work is being undertaken on the interesting low-temperature superlattices formed in the solutions of hydrogen in the Group V metals Ta, V, and Nb. A statistical mechanical model involving a hard short-range H-H repulsive interaction has been shown to be in good accord with the measured thermodynamic functions of the partially ordered systems above the order-disorder transition temperature and also with the geometry of the ordered phase (orthorhombic).

Investigations more directly related to hydrogen-induced failure mechanisms are being undertaken by Dr. F. R. Brotzen. Despite a large volume of experimental data covering many aspects of hydrogen embrittlement, there does not seem to be any clear understanding of the specific nature of the interaction between hydrogen and the metal structure that would explain embrittlement. In previous work a model based on the interaction between dissolved hydrogen and dislocation pile-ups was proposed. In order to quantify this model, the nature of the stress distribution around a dislocation pile-up must be understood. Current investigations are aimed at solving this problem for the case where the dislocations lie concentrically around a circular inclusion. The differences in the moduli of edge and screw dislocations are neglected. Although a satisfactory solution for the radial distribution of dislocations in a circular pile-up has been found, it has not yet been possible

to calculate correctly the coefficients containing the variables of the inner and outer limits of the pile-up. Various approaches are being used to obtain a solution.

A direct investigation concerning the effect of hydrogen on mechanical properties is also being pursued by Dr. J. M. Roberts who is measuring the fracture behavior of single-crystal and polycrystalline samples of molybdenum, doped with 1 ppm of hydrogen. This small amount of hydrogen was found to increase the ductile-to-brittle transition temperature by 125°C for polycrystals and by 50°C for single crystals. The ductile-to-brittle transition for H-doped samples extends over a wider range (200°C) for the polycrystals than for the single crystals (40°C). The data suggest that the onset of brittleness in the polycrystal specimens containing hydrogen may be associated with the early onset of necking at a critical stress value (not strain). In the single crystals however the data indicate that the mechanical behavior after necking is decidedly different between H-doped and H-free specimens.

The tentative conclusion has been drawn that hydrogen, or hydrogen-impurity clusters, appear to become mobile and migrate in the long-range stress fields of dislocation groups in polycrystals. This relaxes the stress internally allowing local recovery to be greater than local hardening. This would account for the early onset of necking. Apparently strong obstacles such as grain boundaries are necessary to initiate local strain instability.

Dr. Roberts plans to carry out a similar program using single and polycrystalline Ta specimens. This should indicate if the results obtained on H-doped molybdenum have more general applicability to the embrittlement of B.C.C. metals by hydrogen.

In addition to the above investigations, Dr. Roberts is initiating an investigation of the effects of H-additions on the surface structure of deformed and fractured tantalum single crystals and polycrystals. At the same time megacycle-range elastic constant measurements will be made on pure and H-doped Ta single crystals.

Dr. F. R. Brotzen and Dr. G. Harkins have jointly been pursuing a study of hydrogen embrittlement and stress corrosion in transition metals. The major portion of this work will consist of the experimental investigation of the H-induced embrittlement of materials using an environmental chamber with the appropriate monitoring equipment for accurate atmosphere control. In addition to the environmental chamber a vacuum extraction chamber featuring grease-free and mercury-free operations is under construction. This facility will enable very accurate residual hydrogen to be measured. Since hydrogen embrittlement can result from the dissolution of such minute quantities of hydrogen in the embrittled material, accurate analytical facilities are necessary in an exhaustive and careful study of environmental embrittlement involving hydrogen.

C. Polymers and Materials at High Temperatures and Pressures

Staff: C. D. Armeniades, Assoc. Professor of Chemical Engineering
L. V. McIntire, Asst. Professor of Chemical Engineering
J. L. Margrave, Professor of Chemistry
J. M. Roberts, Professor of Materials Science

Structural polymers and polymer composites show unusual promise as materials for aerospace applications, because of their high strength-to-weight ratio. However, current use of these materials is limited by their severe embrittlement at low temperatures. This grant contributes to the support of research, which seeks to understand the effects of chemical structure and molecular organization on the mechanical properties of structural polymers at cryogenic temperatures and to develop criteria for optimizing their low-temperature ductility. Theoretical work is also conducted on the phenomenon of melt fracture, which has immediate applications in the extrusion of thermoplastic polymers. In addition, the grant contributes to the support of studies of solids and liquids at high temperatures and high pressures using specially developed instrumentation and techniques. These studies have provided previously unavailable data on the thermodynamic properties and crystal structure of various high-melting metals and alloys, which are important in engine construction. They have also established the structural forms of inorganic compounds at extreme conditions. Activities in these projects during the current period may be summarized as follows:

1) Structure-Property Relations in Semicrystalline Polymers

. This project under the direction of Professors Armeniades and Roberts seeks to relate the low-temperature mechanical properties of selected semicrystalline polymers with their chemical structure and molecular organization, in order to elucidate the stress-transfer mechanism from a macroscopic to a molecular scale. Its results should help provide a rigorous basis for selecting and processing polymeric materials for structural applications in aerospace.

Experimental work during this period involved quantitative determination of the effect of uniaxial orientation (drawing) on the temperature and strength of the internal friction peaks in semicrystalline polyethylene terephthalate. These experiments utilized a recently constructed attachment to the cryogenic torsion pendulum, that permits *in situ* tensile deformation of the specimens, which are then subjected to dynamic mechanical measurements in the same apparatus. It was found that uniaxial drawing causes an upward shift in peak temperature and an increase in the strength of the γ and δ relaxations, in agreement with our earlier theory, which attributes these relaxations to motion of defect structures in the semicrystalline polymer.

Concurrent work is aimed at extending the model, proposed for the motion of defects in linear polymer chains with planar

zig-zag conformations to the helical chain conformations, characteristic of anisotropically substituted polymers in a crystalline lattice. Polychlorotrifluorethylene (PCTFE, known commercially as Kel F) is used as a representative polymer, since it can be prepared (by proper thermal processing) in a wide range of crystalline contents. Preliminary data indicate that this polymer shows a broad relaxation peak around 120°K, the temperature where it was shown in our previous experiments to undergo a transition from ductile to brittle fracture in static tensile tests.

2) Rheological Properties of Polymer Melts

The problem of surface irregularities, generated during polymer melt extrusion has been a bothersome one in thermoplastic melt processing. Empirical evidence has indicated that these instabilities are due to the elasticity of the melt and occur at a critical value of elastic shear strain or recoverable elastic strain. Using techniques of hydrodynamic stability analysis and a constitutive equation for polymer melts, Dr. McIntire has been able to show that this type of instability is predicted to occur theoretically, near the critical value of elastic shear strain (or equivilently Weissenberg number) observed experimentally. This gives a quantitative rationale for the empirical observations and should be helpful in design procedures for melt extrusion equipment.

3) Studies of Solids and Liquids under High Temperatures and High Pressures.

Research in this area is conducted under the direction of Dr. J. L. Margrave. Work during this period involved further refinement of a new polychromatic X-ray diffraction technique and investigation of certain organic and organometallic reactions at high temperatures and pressures. Specific activities are as follows:

(1) X-ray Diffraction Resolution Studies To improve the resolution of output from a new polychromatic X-ray diffraction technique described in previous reports, studies are being conducted on the effects of alterations in the design of sample holders. This method of X-ray analysis is used to examine most materials studied here and particularly in the continuing study of the high temperature orthorhombic to cubic phase transition of PbF_2. Changes in the designs of entrance and exit X-ray collimators in the sample holders have shown that the entrance collimator has little effect on the data output. Alterations in the angle through which the X-rays are diffracted give an initial indication that maximum resolution occurs when the X-rays are diffracted from a straight path through an angle of about 60°.

(2) Crystal Structure Determination Study X-ray powder data in conjunction with a computer program are being used to determine the crystal structure of a powdered high temperature lubricant, CFX. Early results suggest that it has either a monoclinic or an orthorhombic structure.

(3) High Temperature - High Pressure Studies Using a high pressure tetrahedral anvil device various high temperature - high pressure reactions are being attempted.

Diamond synthesis attempts involving the reaction of CFX with various metals have yielded a product whose X-ray pattern corresponds to a diamond structure with a slightly smaller lattice parameter. More of this product must be prepared to further investigate its properties.

The synthesis of a metallic solid possessing a low coefficient of friction is being attempted by sintering a metal powder with CFX. Tests conducted so far have used nickel as the base metal, and a solid, metallic product has been created although its frictional properties have not yet been examined.

Appendix I

Publications During the Period of this Report

A. Data Processing

1. "High Power Broadly Tunable Difference - Frequency Generation in Proustite," C. D. Decker and F. K. Tittel, Appl. Phys. Lett. 22, 411 (1973).

2. "Broadly Tunable, Narrow Linewidth Dye Laser Emission in the Near Infrared," C. D. Decker and F. K. Tittel, Opt. Communications 7, 155 (1973).

3. "Generation of Tunable Coherent Radiation in the Wavelength Range 2300-3000Å Using Lithium Formate Monohydride," F. B. Dunning, F. K. Tittel, and R. F. Stebbings, Opt. Communications 7, 181 (1973).

4. "Difference Frequency Generation by Optical Mixing of Two Dye Lasers in Proustite," C. D. Decker and F. K. Tittel, accepted by Opt. Communications.

B. Hydrogen in Metals and Stress Corrosion Phenomena

1. "Temperature Dependence of Hall Effect and Resistivity in Single Crystals of Mo and Nb and of Mo-Rich Re, Mo-Nb, and Nb-Rich Zr Alloys," W. R. Cox, D. J. Hayes, and F. R. Brotzen, Phys. Rev. B7, 3580 (1973).

2. "Elastic Constants of Niobium-Rich Zirconium Alloys Between 4.2 and 300 K," D. J. Hayes and F. R. Brotzen, accepted for publication J. Appl. Phys.

3. "Solution Thermodynamics," R. B. McLellan, Review Article to be published in "Treatise on Materials Science," ed. H. Herman, Academic Press.

4. "Thermodynamics of F-Transition Metal Solutions," W. J. Arnoult and R. B. McLellan, to appear in Acta Met.

5. "Cumulant Expansions in Ternary Systems," J. C. Langeberg and R. B. McLellan, to appear in Acta Met.

6. "The Convergence of the Cumulant Moment Expansion Technique for Calculating the Free Energy of Solid Solutions," K. Alex and R. B. McLellan, J. Phys. Chem. Solids 34, 1145 (1973).

7. "Solubility of Hydrogen in Rhodium, Ruthenium, Iridium, and Nickel," R. B. McLellan and W. A. Oates, Acta Met. 21, 181 (1973).

8. "Solid Solutions of Hydrogen in Copper, Silver and Gold," R. B. McLellan, J. Phys. Chem. Solids 34, 1137 (1973).

9. "The Influence of Dissolved Hydrogen on the Superconductive Properties of Molybdenum," B. D. Bhardwaj and H. E. Rorschach, to be published in the Proceedings of the 13th International Conference on Low Temperature Physics; (Boulder, Colo. 1973).

10. "Eddy Current Measurements on Ultra-Pure Molybdenum and Rhenium," M. C. Riherd and R. Schreiber, to be published in J. Appl. Phys. (October, 1973).

C. Polymers and Materials at High Temperatures and Pressures

None

Appendix II

Financial Report

NASA Grant NGL 44-006-001

Report of Expenditures

	For the Period 1/1/73	6/30/73	For the Period 5/1/59	6/30/73
Salaries				
Professional	$36,257.40		$1,088,930.32	
Student	4,670.38		529,422.36	
		$40,927.78		$1,618,352.68
Indirect Costs:				
@50% of salaries in the first $150,000 expended			$ 235,429.10	
@25% of direct cost not to exceed $120,000 of the next $600,000 expended			$ 120,000.00	
@20% of direct costs not to exceed $216,666.67 of the next $1,300,000 expended			$ 216,666.67	
@55.6% of salaries except $2,400.00 1/1/73-6/30/73	$21,421.46		$ 135,611.29	
	804.00		804.00	
		$22,225.46		$ 708,511.06
Expendables:				
Supplies & Materials	$24,328.23		$ 675,881.20	
Minor Equipment	1,250.06		212,142.97	
		$25,578.79		$ 888,024.17
Major Equipment		-0-	$ 403,466.24	403,466.24
Commitments Outstanding				
Supplies & Materials	$ 3,544.16		$ 3,544.16	
Minor Equipment	2,401.85		2,401.85	
Major Equipment	15,000.00		15,000.00	
		$20,946.11		$ 20,946.11
Totals		$109,678.14		$3,639,300.26

Grant Reconciliation	
Expended 5/1/59-6/30/73	$3,618,354.15
Budget 7/1/73-6/30/74	241,086.11
Unrecorded award (budget)	290,559.74
Total Grant	$4,150,000.00